

(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) Publication number:

**0 593 771 A1**

(12)

**EUROPEAN PATENT APPLICATION**  
published in accordance with Art.  
158(3) EPC

(21) Application number: **93905629.7**(51) Int. Cl.<sup>5</sup>: **C02F 1/42, C02F 1/28**(22) Date of filing: **10.03.93**(86) International application number:  
**PCT/JP93/00295**(87) International publication number:  
**WO 93/17972 (16.09.93 93/22)**(30) Priority: **13.03.92 JP 89799/92**(43) Date of publication of application:  
**27.04.94 Bulletin 94/17**(84) Designated Contracting States:  
**DE FR GB IT**

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(54) **METHOD OF RECOVERING VOLATILE ACIDS.**

(57) A method of recovering volatile acids and a method of treating wastewater utilizing the above method, the recovery method comprising bringing a waste liquid containing volatile acids into contact with an amine boiling at 50 °C or above to thereby effect ionic adsorption of the acids by the amine and heating the resultant amine to release the adsorbed acids.

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## (TECHNICAL FIELD)

The present invention relates to a process for recovering volatile acids and to a process for treating waste water utilizing this process.

## (BACKGROUND ART)

For example, hydrofluoric acid is recovered from waste liquids containing this acid conventionally by (1) a process wherein fluoride ions are reacted with a calcium, magnesium or like compound to precipitate the ions as a fluoride (JP-A-89984/1983, JP-B-71197/1991, etc.), or (2) a process wherein fluoride ions in the waste liquid are captured by a device having an ion exchange membrane and an ion exchange resin in combination and electrically dialyzed in an electric field to recover hydrofluoric acid (JP-A-123606/1989, JP-A-130782/1989, etc.). However, the process (1) requires decomposition of the fluoride with an acid such as sulfuric acid when hydrofluoric acid is reproduced, necessitating a great apparatus for the filtration of the precipitate and the subsequent decomposition. The process (2) requires a large quantity of electric power, further necessitating the step of separating the recovered acid from other acid, for example, by evaporation or forming the fluoride of calcium, magnesium or the like.

Thus, the prior art has the problems of requiring an additional chemical for recovering hydrofluoric acid and a further treatment of the recovered substance for separation, and consuming a large amount of electric power.

An object of the present invention is to obviate these problems and to provide a process for recovering volatile acids without necessitating additional chemicals and much electric power and without necessitating a separation or decomposition treatment after recovery.

Another object of the invention is to provide a process for treating waste water utilizing the above process.

The present invention provides a process for recovering a volatile acid characterized by bringing a waste liquid containing the volatile acid into contact with an amine having a boiling point of at least 50 °C to thereby cause the amine to ionically adsorb the acid from the waste liquid, and thereafter heating the amine to desorb the acid.

The present invention also provides a waste water treating process characterized in that a waste liquid containing a volatile acid is brought into contact with an amine having a boiling point of at least 50 °C to thereby cause the amine to ionically adsorb the acid from the waste liquid.

The waste liquids containing a volatile acid and to be treated according to the invention include, for example, those containing an acid such as hydrofluoric acid, hydrochloric acid or nitric acid. These waste liquids may further contain sulfuric acid or like nonvolatile component, ammonium fluoride or the like. Such nonvolatile components, even if present, will not affect the volatile acid recovering treatment of the invention but reduce the adsorbing capacity of the amine, so that presence of nonvolatiles in a large quantity is not desirable.

Examples of useful amines having a boiling point of at least 50 °C are anion exchange resins, polyamines, aliphatic amines, aromatic amines and nitrogen-containing heterocyclic compounds. When having a boiling point of below 50 °C, amines themselves will evaporate when heated, and such amines are therefore undesirable. Examples of anion exchange resins are those comprising a copolymer of styrene and divinylbenzene, polyolefin polymer or the like as the base material. Examples of polyamines are 1,8-diaminooctane, 1,1,4,7,10,10-hexamethyltriethylenetetramine, N,N'-bis(3-aminopropyl)-1,3-propanediamine, etc. Examples of aliphatic amines are hexacyclen, hexamethylhexacyclen, etc. Examples of aromatic amines are 2,3-diaminonaphthalene, 9,10-diaminophenanthrene, etc. Examples of nitrogen-containing heterocyclic compounds are 4,7-phenanthroline, carbazole, 29H,31H-phthalocyanine, etc.

According to the invention, the volatile acid is brought into contact with the amine, for example, by passing the waste liquid of volatile acid through a column packed with the amine, or by contacting the waste liquid with the amine batchwise without using a column. The contact thus effected causes the amine to ionically adsorb the volatile acid. With the latter batchwise process, it is necessary to separate the amine from the waste liquid after adsorption and before the subsequent step of heating, whereas the amine need not be so separated off with the former column process.

The adsorbed volatile acid is released from the amine by heating. The amine is heated by a desired method. For example, it is heated as contained in the column or with hot air passed through the column. It is desired that the heating temperature be such that the amine remains unaffected by heat to the greatest possible extent, that is, not higher than the limit within which the amine retains its function. The amine is heated until the component released therefrom becomes neutral in pH value. The preferred heating time is

usually in the range of 1 minute to 50 hours.

With the process of the invention, the heating temperature is usually about 50 to about 180 °C, preferably about 70 to about 130 °C.

The present process is usable for treating waste water to remove volatile acids therefrom even if the concentration of the acid is low and can not be recovered efficiently. More specifically, the waste water treating process is conducted, for example, by a system comprising two columns arranged in parallel, packed with an amine and each connected to waste water, acid recovery and steam lines. The two columns are operated alternately. While one of the columns is treating waste water, the other column is used for recovering (regenerating) the acid in preparation for the subsequent treatment. When saturated with the adsorbed acid by passing waste water, the column is changed over to the other column. The saturated column is heated as by passing steam therethrough to recover the acid. Waste water can be treated continuously by repeating the above procedure.

(BEST MODE FOR CARRYING OUT THE INVENTION)

The present invention will be described in detail with reference to the following examples.

#### Example 1

Hydrofluoric acid was recovered by the following process using the anion exchange resin stated below as an amine. Table 1 shows the result.

Anion exchange resin

Base material: styrene-divinylbenzene copolymer  
Exchange group:  $-\text{CH}_2\text{N}(\text{CH}_3)_2$   
Exchange capacity: at least 1.5 meq/ml  
Apparent density: 615 g/l  
Effective particle size: 0.4~ 0.6 mm

(1) A 4.1 g quantity of the anion exchange resin was placed into 20 g of 2 % aqueous hydrofluoric acid solution (0.02 mole). The mixture was stirred, and filtered about 5 minutes later. The filtrate was checked for HF concentration. The difference between the amount of HF used and the amount of HF in the filtrate was taken as the amount of HF adsorbed.

(2) The anion exchange resin was washed with water and thereafter placed into a platinum dish, which was then heated on a hot plate at 100 °C for 2 hours.

(3) After heating, 10 g of 2.27N aqueous NaOH solution was added to the anion exchange resin, followed by stirring and, about 5 minutes later, by filtration. The filtrate was titrated with 2.5N hydrochloric acid to determine the amount of remaining HF. The difference between the amount of adsorption and the remaining amount was taken as the amount of HF released.

(4) After washing the resin with water, the step (1) was repeated again to determine the amount of adsorption.

(5) The above procedure was repeated to check the resin for variations in the amount of HF thereby adsorbed and for durability.

Table 1

Variations in the Amount of Adsorbed HF after Heat Treatment		
Repetition	Adsorbed HF measurement (mole)	Relative ratio (%)
Initial	$1.62 \times 10^{-2}$	100
First	$1.44 \times 10^{-2}$	89
Second	$1.39 \times 10^{-2}$	86
Third	$1.36 \times 10^{-2}$	84
Note: The relative ratio was based on the initial adsorption measurement which was taken as 100. The amount of HF released was at least 90 % of the amount of adsorption each time.		

Example 2

Hydrofluoric acid was recovered by the same process as in Example 1 using the polyamine beads described below. Table 2 shows the result.

## Polyamine beads

Base material: straight-chain olefin polymer (crosslinked beads)  
 Exchange group:  $-\text{CH}_2\text{NH}_2$   
 Exchange capacity: 15 meq/g (dry)  
 Size of beads: 48– 145 mesh

This experiment was conducted in the same manner as in Example 1 with the exception of using the polyamine beads which corresponded to 0.01 mole in exchange capacity and heating the beads at about 85 °C.

Table 2

Variations in the Amount of Adsorbed HF after Heat Treatment		
Repetition	Adsorbed HF measurement (mole)	Relative ratio (%)
Initial	$9.84 \times 10^{-3}$	100
First	$8.62 \times 10^{-3}$	88
Second	$7.20 \times 10^{-3}$	73
Third	$6.33 \times 10^{-3}$	64
Note: The relative ratio was based on the initial adsorption measurement which was taken as 100. The amount of hydrofluoric acid released was at least 70 % of the amount of adsorption each time.		

Example 3

Hydrochloric acid was recovered using the same anion exchange resin as in Example 1. Table 3 shows the result. This experiment was carried out in the same manner as in Example 1 with the exception of using 20 g of hydrochloric acid having a concentration of 3.6 % (0.02 mole) and 3.6 g of the anion exchange resin and heating the resin at 100 °C.

Table 3

Variations in the Amount of Adsorbed HCl after Heat Treatment		
Repetition	Adsorbed HCl measurement (mole)	Relative ratio (%)
Initial	$8.92 \times 10^{-3}$	100
First	$4.15 \times 10^{-3}$	47
Second	$4.04 \times 10^{-3}$	45
Third	$3.07 \times 10^{-3}$	34
Note: The relative ratio was based on the initial adsorption measurement which was taken as 100. The amount of HCl released was at least 90 % of the amount of adsorption each time.		

## (INDUSTRIAL APPLICABILITY)

According to the invention, volatile acids are adsorbed by an amine, which is then heated for the recovery of the acid, so that volatile acids can be recovered by an inexpensive simple apparatus. As

compared with conventional processes, e.g., the recovery process wherein a fluoride is formed, the invention can be practiced by a compacted apparatus without using an acid for decomposition. Further unlike the electric dialysis process, a particular volatile acid only can be recovered selectively. The volatile acid can therefore be recovered with a high purity and at a high concentration (almost about 100 % ).

#### Claims

1. A process for recovering a volatile acid characterized by bringing a waste liquid containing the volatile acid into contact with an amine having a boiling point of at least 50 °C to thereby cause the amine to ionically adsorb the acid from the waste liquid, and thereafter heating the amine to desorb the acid.
2. A process as defined in claim 1 wherein the volatile acid is hydrofluoric acid.
3. A process as defined in claim 1 wherein the amine having a boiling point of at least 50 °C is an anion exchange resin, polyamine, aliphatic amine, aromatic amine or nitrogen-containing heterocyclic compound.
4. A waste water treating process characterized in that a waste liquid containing a volatile acid is brought into contact with an amine having a boiling point of at least 50 °C to thereby cause the amine to ionically adsorb the acid from the waste liquid.
5. A waste water treating process as defined in claim 4 wherein the amine having a boiling point of at least 50 °C is an anion exchange resin, polyamine, aliphatic amine, aromatic amine or nitrogen-containing heterocyclic compound.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP93/00295

A. CLASSIFICATION OF SUBJECT MATTER		
Int. Cl <sup>5</sup> C02F1/42, 1/28		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols)		
Int. Cl <sup>5</sup> C02F1/42, 1/28		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Jitsuyo Shinan Koho 1926 - 1993		
Kokai Jitsuyo Shinan Koho 1971 - 1993		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, A, 58-8582 (Hitachi Plant Engineering and Construction Co., Ltd.), January 18, 1983 (18. 01. 83), Lines 2 to 20, lower right column, page 1 (Family: none)	1-5
A	JP, A, 57-15885 (Nippon Rensui Co., Ltd.), January 27, 1982 (27. 01. 82), Line 7, lower right column, page 2 to line 9, upper left column, page 3 (Family: none)	1-5
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search		Date of mailing of the international search report
June 1, 1993 (01. 06. 93)		June 22, 1993 (22. 06. 93)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)